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FINAL TECHNICAL REPORT

During the three years of this grant, a negative ion time-of-flight photoelectron spectrometer was constructed and used in a series of novel experiments designed to probe the transition state region in chemical reactions. In addition, conventional photoelectron spectra of several anions with high electron binding energies were obtained. The design of the instrument and the two types of experiments are described in more detail below.

A) DESIGN OF PHOTOELECTRON SPECTROMETER

The key features of the photoelectron spectrometer are as follows. Cold negative ions are produced in an ion source based on a pulsed free jet expansion. The ions are mass-selected using a time-of-flight mass spectrometer. Ions of the desired mass are then photodetached with a pulsed, fixed-frequency laser, and the kinetic energy distribution of the ejected photoelectrons is determined by a second time-of-flight system. This allows us to map out the vibrational and electronic energy levels of the neutral species created by photodetachment of the mass-selected anions.

In more detail, cold anions are formed by crossing a pulsed molecular beam with a 1 keV electron beam 0.1-1 cm downstream of the beam orifice. This results in negative ion formation in the continuum flow region of the free jet expansion, with cooling of the ions occurring as the expansion progresses. Negative ions are extracted from the beam by means of a pulsed electric field and are injected into a 140 cm long time-of-flight mass spectrometer, where they separate into bunches according to their mass. The mass-

selected anions are photodetached using a Nd:YAG laser from which wavelengths up to the fifth harmonic (213 nm) of the 1064 nm fundamental can be obtained. This gives us a maximum photon energy of 5.825 eV. A small fraction of the ejected photoelectrons is detected 1 m from the laser/ion beam interaction region; the kinetic energy distribution of these electrons is determined by measuring their arrival time distribution (with respect to the laser pulse) at the detector. This system has an energy resolution of 8 meV at an electron kinetic energy (eKE) of 0.65 eV and degrades as $(eKE)^{3/2}$ at higher kinetic energies.

B) TRANSITION STATE SPECTROSCOPY EXPERIMENTS

In these experiments, the spectroscopy of the transition state of the reaction $A + HB \rightarrow HA + B$ is studied by photodetachment of the stable, hydrogen-bonded AHB^- anion. The idea behind the experiment is that if the anion geometry is similar to that of the neutral transition state, then anion photodetachment allows us to initiate the corresponding neutral reaction in a much more defined manner than can be done in a scattering experiment. Even though the neutral AHB complex resulting from photodetachment is unstable, the AHB^- photoelectron spectrum exhibits resolved vibrational structure associated with the AHB complex in many cases. From this structure, we obtain detailed information on the transition state region of the potential energy surface for the neutral reaction and learn about the microscopic forces that govern chemical reactivity.

Most of these studies were performed on "heavy + light-heavy" reactions in which a hydrogen atom is transferred between two much

heavier species. Our first studies focussed on the symmetric Cl + HCl, Br + HBr, and I + HI reactions, which were studied by photoelectron spectroscopy of ClHCl⁻, BrHBr⁻, and IH⁻, respectively. This was followed by studies the asymmetric X + HY reactions, where X and Y are two different halogen atoms. In addition, we investigated the polyatomic F + CH₃OH → HF + CH₃O reaction and the analogous F + C₂H₅OH reaction via photoelectron spectroscopy of the CH₃OHF⁻ and C₂H₅OHF⁻ reactions, respectively. In all of the above studies, the anion photoelectron spectrum showed progressions in the "v₃" mode of the AHB complex, in which the H atom is vibrating between the much heavier A and B moieties. More recently, we have investigated the F + H₂ reaction, which is not a heavy + light-heavy reaction, via photoelectron spectroscopy of the FH₂⁻ anion. This work is continuing during the current grant period.

This research program represents one of the few successful approaches to transition state spectroscopy and has received considerable attention in the scientific community. In particular, several theoretical chemists (George Schatz, Joel Bowman, Bill Miller, and others) have developed methods to simulate these photoelectron spectra using various model potential energy surfaces for the reaction in question. This will ultimately result in the development of chemically accurate surfaces for these reactions.

C) "CONVENTIONAL" PHOTOELECTRON SPECTROSCOPY EXPERIMENTS

We have also performed more conventional photoelectron spectroscopy experiments in which a stable neutral species is

formed by anion photodetachment. Our maximum photon energy (5.825 eV) is considerably higher than the cw-laser based instruments on which most anion photoelectron spectra have been obtained to date (3.5 eV). This means we can study anions with higher electron binding energies and access excited electronic states of the neutral. Our studies of the photoelectron spectra of NO₂⁻ and NO₃⁻ are examples of this type of study; in both cases, for example, we observed "dark" excited electronic states of the neutral which had not been seen previous.

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COMPLETED PROJECT SUMMARY

TITLE: Spectroscopy of the Transition State Region in Chemical Reactions

PRINCIPAL INVESTIGATOR: Daniel M. Neumark

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CONTRACT/GRANT NO: AFOSR-87-0341

SENIOR RESEARCH PERSONNEL: none, other than P.I.

JUNIOR RESEARCH PERSONNEL: Alexandra Weaver, Ricardo Metz, Stephen Bradforth, Don Arnold

PUBLICATIONS ACKNOWLEDGING THIS GRANT:

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The spectroscopy of the transition state region for several hydrogen transfer reactions of the type $A + HB \rightarrow HA + B$ was studied via photoelectron spectroscopy of the stable anion AHB^- anion. Reactions included the symmetric $Cl + HCl$, $Br + HBr$, and $I + HI$ reactions, triatomic reactions such as $Br + HI \rightarrow HBr + I$ and $F + H_2 \rightarrow HF + H$, and the polyatomic reactions $F + CH_3OH \rightarrow HF + CH_3O$ and $F + C_2H_5OH \rightarrow HF + C_2H_5O$. In the experiments, cold precursor anions ($ClHCl^-$, FH_2^- , CH_3OHF^- , etc.) are generated in an ion source base on a pulsed molecular beam, mass-selected using time-of-flight, and photodetached with one of the harmonics of a Nd:YAG laser. The resulting photoelectron energy distribution is determined by time-of-flight.

All of the anion photoelectron spectra show resolved vibrational structure characteristic of the transition state region of the potential energy surface for the neutral reaction. This has resulted in the development of new surfaces for several of these reactions. Ultimately, these studies will provide new insight into the microscopic, interatomic forces that govern chemical reactivity.

List of Publications

1. R. B. Metz, T. Kitsopoulos, A. Weaver, and D. M. Neumark, "Study of the transition state region in the Cl + HCl reaction by photoelectron spectroscopy of ClHCl⁻," J. Chem. Phys. 88, 1463-1465 (1988).
2. A. Weaver, R. B. Metz, S. E. Bradforth, and D. M. Neumark, "Spectroscopy of the I+HI Transition State Region by Photodetachment of IHI⁻," J. Phys. Chem. 92, 5558-5560 (1988).
3. A. Weaver, R. B. Metz, S. E. Bradforth, and D. M. Neumark, "Observation of the A(²B₂) and C(A₂) States of NO₂ by Negative Ion Photoelectron Spectroscopy of NO₂⁻," J. Chem. Phys. 90, 2070-2071 (1989).
4. R. B. Metz, A. Weaver, S. E. Bradforth, T. N. Kitsopoulos, and D. M. Neumark, "Probing the Transition State with Negative Ion Photodetachment: The Cl + HCl and Br + HBr Reactions," J. Phys. Chem. 94, 1377-1388 (1990).
5. S. E. Bradforth, A. Weaver, D. W. Arnold, R. B. Metz, and D. M. Neumark, "Examination of the Br + HI, Cl + HI, and F + HI Hydrogen Abstraction Reactions by Photoelectron Spectroscopy of BrHI⁻, ClHI⁻, and FHI⁻," J. Chem. Phys. 92, 7205-7222 (1990).
6. D. M. Neumark, "Transition State Spectroscopy of Hydrogen Transfer Reactions," in Electronic and Atomic Collisions: Invited Papers of the XVI ICPEAC (AIP Conference Proceedings No. 205), edited by A. Dalgarno, R. S. Freund, P. Koch, M. S. Lubell, and T. B. Lucatorto (American Institute of Physics, New York: 1990), pp. 33-48.
7. D. M. Neumark, "Negative Ion Photodetachment as a Probe of the Transition State Region: The I + HI Reaction," in Advances in Molecular Vibrations and Collision Dynamics (JAI, in press).
8. A. Weaver, R. B. Metz, S. E. Bradforth, and D. M. Neumark, "Investigation of the F + H₂ Transition State Region Via Photoelectron Spectroscopy of the FH₂ Anion," J. Chem. Phys. 93, 5352-5353 (1990).
9. A. Weaver, D. W. Arnold, S. E. Bradforth, and D. M. Neumark, "Examination of the 'A₂' and 'E' States of NO₃ by Ultraviolet Photoelectron Spectroscopy of NO₃⁻," J. Chem. Phys. 94, 1740-1751 (1991).